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BORON NITRIDE FOR MICROCOMPOSITE CERAMICS PRODUCED BY PROTON-CARBON TREATMENT

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The possibility of obtaining wurtzite-like boron nitride with a microcomposite structure in the form of nanotube packets using low-temperature proton-carbon treatment is investigated. It is demonstrated that the formation of nanotube packets at a distance from the treatment zone is related to the collective shift deformations of the layers consisting of self-organizing blocks.

Microcomposite ceramic materials are currently widely used in industry. They have a number of advantages compared to composite ceramics based on BN, primarily, a high level of charge transfer and microplasticity, which allow for production of electrotechnical and structural materials. Owing to the anisotropic nature of the charge transfer and microplasticity phenomena, a controlled conductivity and a decrease in the temperature of deformation relaxations can be ensured.

Of special interest are nanoceramics based on nanotubes made of a microcomposite material which ensures self-organized transfer and microplasticity at temperatures which are close to room temperature. The published sources describe the procedures of production of carbon and BN nanotubes and their filling with a doping material [1, 2]. The researchers established as well the effect of liquid oxidizers, electron beams, and laser radiation on the formation of nanotubes [1 – 4].

The purpose of the present study was to obtain self-organizing mesoscopic blocks in wurtzite-like BN_w and to increase the strength of boron pyronitride with the hexagonal structure BN_h using low-temperature proton-carbon treatment. For this purpose, it is necessary to form a microcomposite structure of BN_w blocks based on self-organizing mesoscopic particles (SM-particles) which ensure the collective forms of charge transfer and microplasticity.

The x-ray structural analysis of the initial BN_h and the wurtzite-like BN_w was performed using a DRON-3 diffractometer with Cu-K_β radiation. To restore such structure of subreflections, the method of unfocused Laue diffraction patterns was used, when the sample is shifted from the goniometer center towards the x-ray source, and the diffraction image is observed from the immobile sample as in Laue diffraction patterns. The microscope analysis was performed using an EM-125K electron microscope.

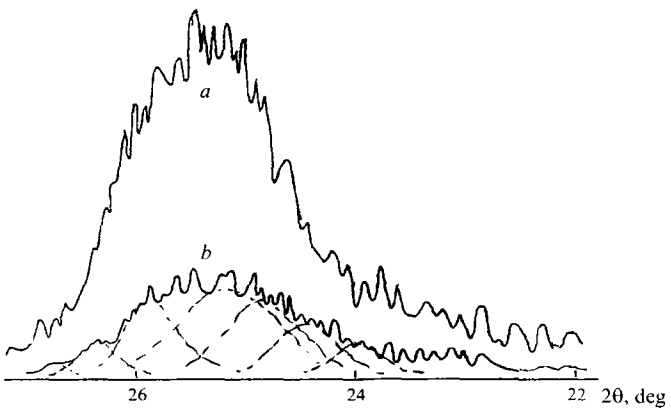

Fig. 1. Fine structure of diffraction reflection (002) of initial BN (*a*) and BN after proton-carbon treatment (*b*).

TABLE 1

Parameter	Plane (110)	Plane (001)	Fibonacci series step
Size of mesoscopic blocks in BN_w, Å:			
experimental	13.70	36.60	3
	26.14	64.00	4
	95.96	115.60	7
estimated	13.65	36.40	5
	22.75	59.15	6
	95.55	95.55	7

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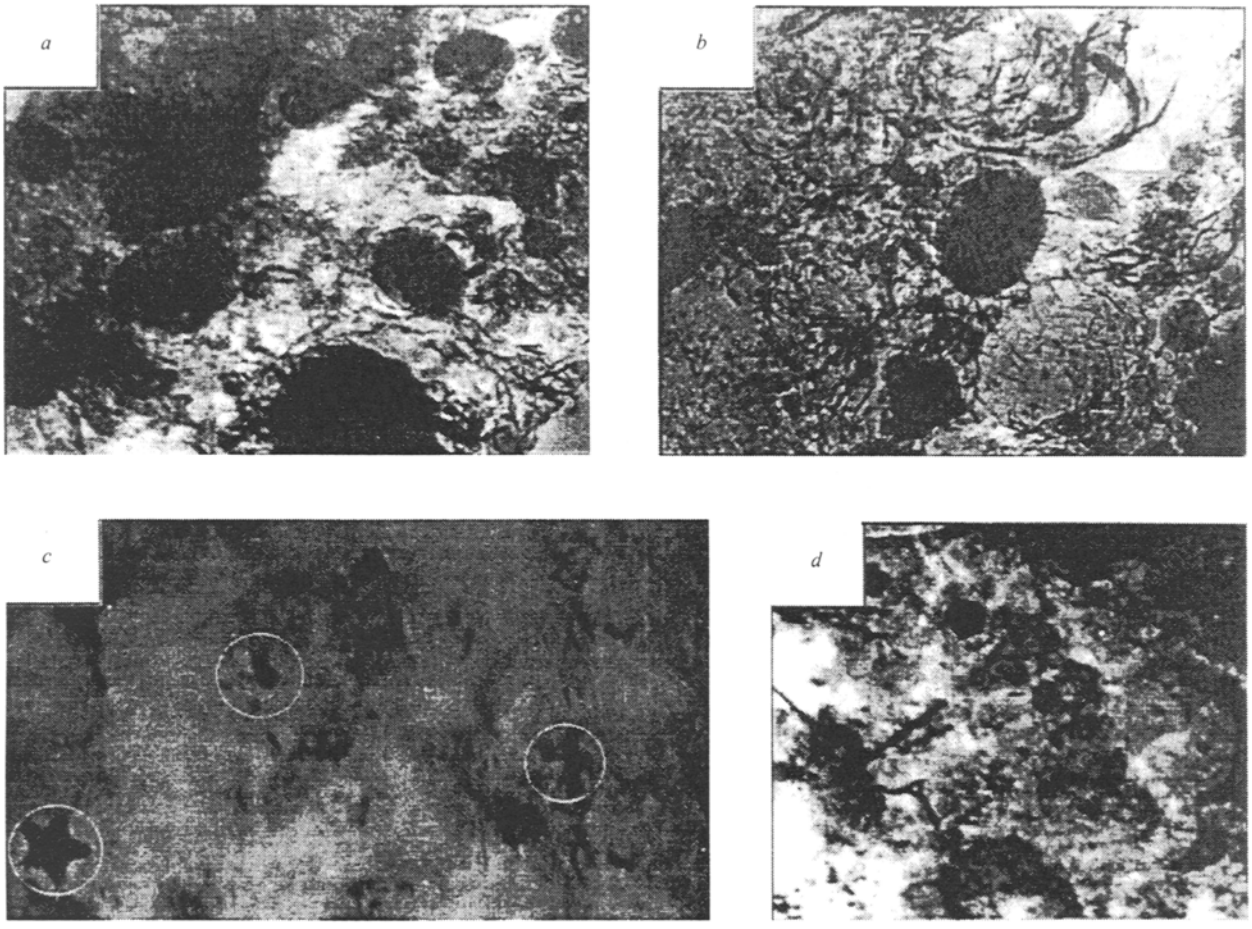

Fig. 2. Electron microscope photos of BN after proton-carbon treatment at a depth of 0 μm (*a*, *b*) and 500 μm (*c*, *d*) for different treatment regimes: *a*) $N = 1000$ pulses, $I = 10$ A/cm^2, $t = 100$ nsec; *b* – *d*) $N = 3$ pulses, $I = 80$ A/cm^2, $t = 20$ nsec; *a*, *b*, *d*) ×80,000; *c*) ×120,000.

The initial BN_h and the boron nitride treated by nanosecond proton-carbon beams ($E = 120$ keV, $I = 10 - 80$ A/cm^2, $t = 20 - 100$ nsec, $T = 15$ pulse/min; $H^+ : C^+ = 40 : 60$) exhibit a complicated image of the distribution of diffraction line integral intensities, which is indicative of a specific distribution of the electron density in the atomic planes (Fig. 1). The nonuniformity of the electron density can be related to redistribution of old mesoscopic blocks and formation of new ones. Each reflection was split into seven subreflections nonperiodically located within a large reflection. Based on the geometry of the arrangement of subsubreflections and subreflections, the dependences of inter-angle positions distribution have the form

$$\Delta\varphi_0\tau^0, \Delta\varphi_0\tau^1, \Delta\varphi_0\tau^2; \quad (1)$$

$$\Delta\varphi_0\tau^0, \Delta\varphi_0\tau^1, \Delta\varphi_0(1/2\tau^2), \Delta\varphi_0(1/3\tau^2), \quad (2)$$

where $\Delta\varphi_0$ is the minimum inter-angle distance; τ is the golden section number.

Table 1 shows the experimental values of the mesoscopic blocks along the planes (110) and (001), taking into account Eqs. (1) and (2). Using the experimentally found interplanar distance value of the plane with the maximum line intensity d_{max}, the size of the SM-particle edge was determined from the expression

$$a = d_{max} N^{1/2} \tau^{1/6} K_{\phi}^{-1/3}, \quad (3)$$

where $N = H^2 + K^2 + L^2$ is the sum of the squares of the most packed plane indexes; K_f is the shape coefficient of SM particles ($K_{cube} = 1$; $K_{oct} = 0.4714$, $K_{tetr} = 0.1179$)

TABLE 2

Nanotube packet parameter	Initial	At a distance from the treatment zone, mm		
		0	10	15
Size of d, nm	8.4	82.0	64.5	6.6
d_{max} (d_{min})	600.0(37.5)	250.0(37.5)	87.5(50.0)	87.5(50.0)
Volume part ΔV, %	~ 1.0	35.0 – 45.0	3.0 – 5.0	≤ 1.0

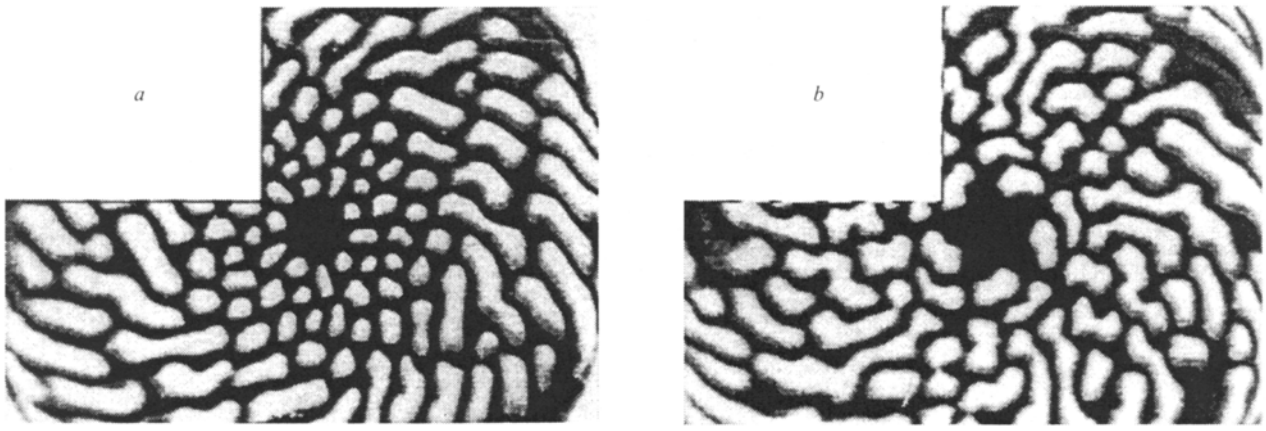

Fig. 3. Nanotubes opening in the form of pentagons (*a*) and stars (*b*) in mesoscopic block packing in a model self-organizing structure.

The estimated values of SM-blocks are obtained based on the accepted assumption for SM-particles which comprise these blocks, and their scaling according to the Fibonacci series. When using octahedral SM-particles with an edge size equal to 4.55 Å, part of the blocks are close in size to the estimated values (Table 1). Larger blocks are formed along the plane (001) under proton-carbon treatment, and part of them are arranged in self-organizing chains (5 – 6 – 7) with self-similar transitions. The experimentally observed blocks whose sizes are 3.10, 3.94, 4.25, and 11.56 nm impede the implementation of such transitions. The distribution of regularly arranged blocks 10 – 20 μm in size was recorded using the topographic registration method according to Scholtz.

Treatment of the initial BN_h using nanosecond beams with high power density is accompanied by the formation of a new wurtzite-like phase. The dependence of the volume part of BN_w has clearly expressed gaps corresponding to a depth of 1.6, 3.2, 4.8, and 7.9 μm. Structural variations are also observed under the shielding screen at a distance of 15 mm from the treatment zone. The low-temperature transformation of $BN_h \rightarrow BN_w$ is related to a decrease in the edge length of the SM-particles by $\Delta a = 0.009$ nm, as well as to the shift deformation of the layers, and the emergence of nanotubes.

The electron microscopic studies confirm the formation of BN_w nanotubes at a sufficient distance from the treatment zone and the change in the distribution of nanotube spheroid packets by depth (Fig. 2). Table 2 shows the ratios of the nanotube packet sizes and the density of their distribution over the sample and at a certain distance from the treatment zone. At a depth of 0.2 μm and at a distance of 15 mm from the treatment zone, the nanotube packets become smaller and their share decreases to 45%. At a depth of ~ 50 μm, BN_w nanotube packets with fifth order symmetry are observed in pentagonal form up to 32 nm in size, and at a depth of ~ 500 μm, they change over to star-shaped nanotube packets up to 62.5 in size.

The mechanism of BN_w nanotube formation can be related to the specifics of self-organization of spiral-cyclic structures [5]. Figure 3 shows the experimentally observed block packing in a self-organizing structure with fifth-order symmetry axis and the formation of pentagons and stars at the exit points of the L_5 axis.

The BN_w nanotubes produced by low-temperature proton-carbon treatment possess all the properties inherent to microcomposite structures and can be used as a component determining the properties of ceramic material in microcomposite ceramics and in coatings whose electrical and mechanical properties are controlled by the thickness.

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